

# Energy-scanned Photoelectron Diffraction Determination of the Structure of Oxygen on Cu{100} at Low Coverage

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## INTRODUCTION

The presence of atomic adsorbates above a critical coverage leads to the reconstruction of many common transition metal surfaces. To gain an understanding of the driving force of such reconstructions it is informative to study the atomic adsorption site prior to the reconstruction. For example, using energy-scanned photoelectron diffraction (PhD) recorded at the ALS we have previously determined the local adsorption site of C on Ni{100} at low coverage (0.15 ML) and in the clock-reconstructed (2x2)p4g phase. The results show that the reconstruction is not driven by expansion strain as previously suggested, but rather the structural data imply that the reconstruction is caused by the relief of C-induced Ni-Ni repulsions [1].

In this report we detail the preliminary results of a quantitative structural study of O on Cu{100} at a coverage of 0.1 ML. At higher O coverages the surface undergoes a missing row reconstruction to give, at a coverage of 0.5 ML, a ( $\sqrt{2}\times\sqrt{2}$ )R45° structure. In the reconstructed phase the O atoms are located at the former hollow sites next to the missing rows. There have been two STM studies of the phase prior to the reconstruction. In a study by Leibsle it was proposed that Cu-O-Cu rows were formed [2], while a later study by Fujita et al refuted this suggestion and claimed instead that the O atoms lay in 4-fold hollow sites in small c(2x2) domains consisting of about four O atoms [3].

To get quantitative structural information on atomic adsorption sites at very low coverage, when there is no long-range order, we use the technique of photoelectron diffraction in the scanned-energy mode (PhD). In PhD the intensity of an adsorbate core level photoemission peak, in this case O 1s, is measured as a function of kinetic energy in several different emission directions. Modulations in the intensity arise from interference between the directly emitted component of the photoelectron wavefield and components which are elastically scattered from neighbouring atoms. The modulations thus depend on the local environment of the adsorbate. By comparing the experimental modulations with the results of multiple-scattering simulations for model adsorbate geometries, quantitative structural information can be derived.

## EXPERIMENT

The PhD measurements for 0.1 ML O on Cu{100} were performed at the UltraESCA endstation of beamline 7.0.1. The high flux and high spectral resolution provided by the ALS are essential to get an adequate signal-to-noise ratio when studying adsorbates at low coverage. Moreover, it is possible to measure emission at very grazing angles, up to 70° away from the surface normal, allowing backscattering from near-coplanar substrate atoms to be detected.

The Cu{100} crystal was cleaned by Ar ion bombardment and anneal cycles. The surface order and cleanliness were checked with LEED and soft X-ray (synchrotron radiation) photoelectron

spectroscopy respectively. The coverage of O was calibrated using the O 1s intensity assuming a coverage of 0.5 ML when a sharp, intense  $(\sqrt{2} \times \sqrt{2})R45^\circ$  LEED pattern was seen. PhD spectra were recorded at room temperature for a wide range of polar angles in the two principal azimuths of the surface. Each PhD spectrum consisted of 146 electron distribution curves (EDCs) centred about the O 1s photoemission peak. For successive EDCs the wavevector of the incident light was incremented by 0.05 from a starting value of 3.6 to an end value of 10.9. The O 1s photoemission peak thus covered the kinetic energy range 50 to 450 eV.

The intensity modulation functions were obtained from the raw data by integrating the EDCs and then normalising the resulting intensity versus kinetic energy curves using a spline function to model the non-diffractive intensity.

## PRELIMINARY RESULTS

The first stage of data analysis involves applying the so-called projection method [4] to determine the approximate adsorption site. The projection method works by effectively picking out the dominating backscattering modulations and comparing these with single-scattering calculations for a substrate atom at different test sites on a 3-D grid below the emitter. The maxima in the projection method map shown in Fig. 1 correspond to the most likely positions of the backscattering substrate atoms. There are two possible interpretations of the projection method map. The four maxima could represent four surrounding Cu atoms for the O atom in a 4-fold hollow site. Alternatively the maxima could represent the Cu atoms of Cu-O-Cu added rows which have a random distribution along the [001] and [010] directions.

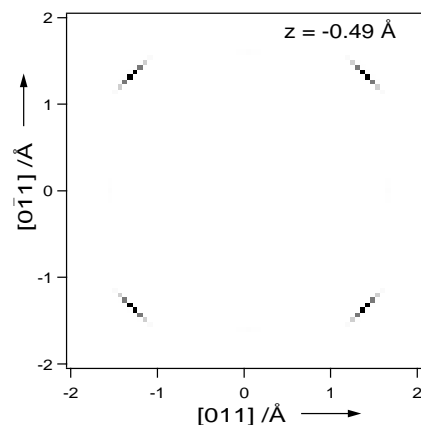


Figure 1. Projection method map showing the likely positions of the nearest neighbour backscattering atoms for a horizontal cut 0.49 Å below the O atom which is at (0,0,0).

The second stage of data analysis involves comparing the experimental modulation functions to the results of multiple-scattering simulations for trial adsorbate structures. The PhD data (the full lines in Fig. 2) show strong modulations at  $60^\circ$  and  $70^\circ$  off-normal which implies backscattering from near-coplanar surrounding Cu atoms. If the O atoms are at a well-defined height low in 4-fold hollow sites then, at normal emission, there should be significant backscattering from the second layer Cu atom directly below the O atom. The normal emission spectrum, however, shows only weak modulations. One possibility is that there is static or dynamic disorder perpendicular to the surface which dampens the normal emission modulations. Assuming there is only one adsorption geometry for the O atom in the 4-fold hollow site, a good fit between experiment and theory (giving an R-factor of 0.21) can only be obtained if the O atom is given a large perpendicular vibration. A slightly better fit (with an R-factor of 0.19) is obtained without the need for an unusually large perpendicular vibration by assuming that there are two possible adsorption geometries for the O atoms in the 4-fold hollow sites. In one of the adsorption sites the O atom is located 0.65 Å above the surrounding four first layer Cu atoms which are moved down by 0.13 Å relative to the other first layer atoms. The second layer Cu atom directly below the O atom is moved up by 0.3 Å. In the second geometry the O atom is only 0.49 Å above the four surrounding first layer Cu atoms. In this case the surrounding first

layer Cu atoms are moved down by 0.13 Å while the second layer atom below is moved up by 0.23 Å. A comparison between the experimental modulation functions and the simulations for the two-site model is shown in Fig. 2.

The multiple-scattering analysis of the data is still continuing. In particular the possibility of added Cu-O-Cu rows is being investigated. Also, a new more detailed analysis of the  $(\sqrt{2}\times\sqrt{2})R45^\circ$  structure is being undertaken to enable a suitable comparison to be made of the structural parameters before and after the reconstruction.

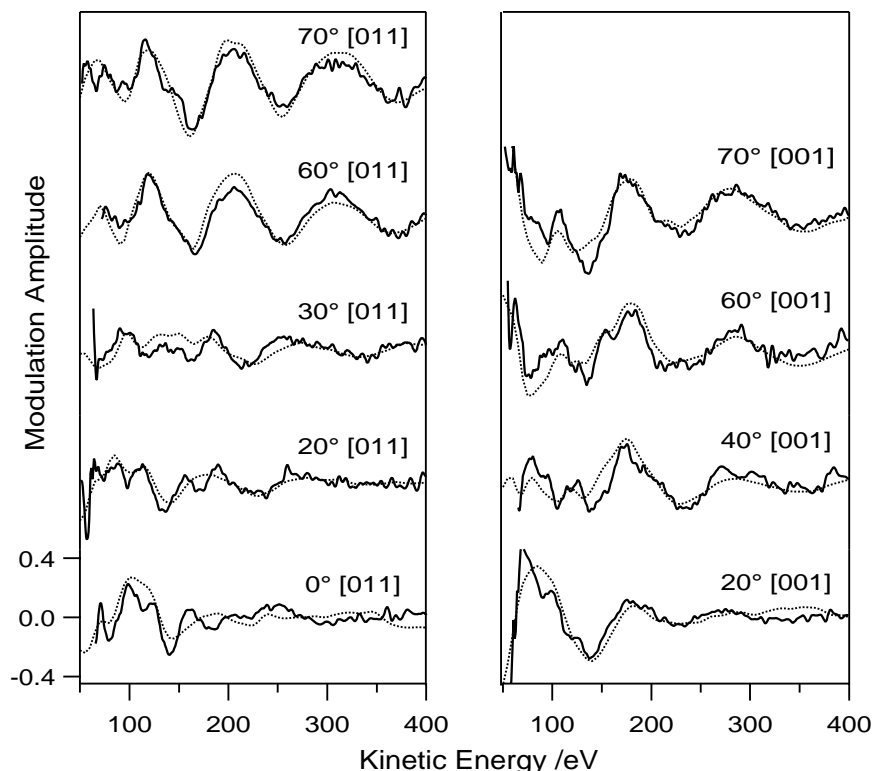


Figure 2. Comparison between the experimental O 1s modulation functions for 0.1 ML O on Cu{100} (full lines) and the simulation for the O atoms distributed in two geometries in the 4-fold hollow sites (dashed lines).

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